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<p>(21) International Application Number: PCT/EP00/00290 (22) International Filing Date: 12 January 2000 (12.01.00) (30) Priority Data: 99200097.6 18 January 1999 (18.01.99) EP 99200492.9 22 February 1999 (22.02.99) EP (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): BÖTTGER, Christian [DE/DE]; Geschwister-Scholl-Strasse 25, D-42897 Remscheid (DE). FELS, Achim [DE/DE]; Adalbert-Stifter Weg 8, D-42109 Wuppertal (DE). DORLOFF-LUMPE, Bärbel [DE/DE]; Falkenberg 119, D-42113 Wuppertal (DE). BAUMGART, Christoph [DE/DE]; Martin Luther Strasse 11C, D-42285 Wuppertal (DE). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: PENETRATION-RESISTANT MATERIAL COMPRISING FABRIC WITH HIGH LINEAR DENSITY RATIO OF TWO SETS OF THREADS</p> <p>(57) Abstract</p> <p>The invention pertains to a penetration-resistant material comprising at least a double layer of fabric composed of two layers of woven fabric which are cross-plyed at an angle, characterized in that the fabric is composed of a first set of threads comprising 3.5 to 20 threads/cm and having a linear density of at least 420 dtex, and a second set of threads comprising 0.5 to 8 threads/cm and having a linear density of at least 50 dtex, with the second set of threads being transverse to the first set of threads, and wherein the ratio of the linear density of the first set of threads to the linear density of the second set of threads is > 4.2, more preferably > 7.5. In a preferred embodiment the first set of threads is warp threads made of p-aramid yarn and the second set of threads is weft threads of polyester yarn, and the ratio of the number of threads/cm of the first set to that of the second set is > 1.</p>		

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PENETRATION-RESISTANT MATERIAL COMPRISING FABRIC WITH HIGH
LINEAR DENSITY RATIO OF TWO SETS OF THREADS

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The invention pertains to penetration-resistant material comprising a fabric with high linear density ratios of two sets of threads, and to articles made of the same.

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Penetration-resistant articles such as bulletproof vests, helmets, vehicle panels, and shields prepared from high strength fibers are known in the art. For many applications, in particular for ballistic vests, the fibers are used in a woven or knitted fabric. These fabrics may be coated or impregnated in a matrix to obtain hard ballistic materials, or may be used free from matrix to obtain soft ballistic materials.

Bulletproof woven fabrics are known, *inter alia*, from EP 310,199. The fabrics disclosed therein are composed of filament yarns of ultrahigh molecular weight polymer having high strength and high modulus, with the warp threads being of a different polymeric material than the weft threads.

In Russian patent RU 2,096,542 a ballistic fabric for bulletproof jackets was disclosed having warp and weft threads of poly para-phenyleneterephthalamide (PPTA) wherein the ratio of warp to weft linear density is smaller than 4.17. Typically, warp threads having a linear density of 143 to 588 dtex and weft threads having a linear density of 588 to 930 were disclosed, the weft threads having equal or higher linear density than the warp threads. It is particularly contended that ballistic fabrics having warp to weft linear density ratios between 1.59 and 4.17 have improved deflection properties.

It has now been found that penetration-resistant materials comprising at least a double layer of fabric composed of two layers of woven fabric which are cross-plied at an angle, characterized in that the fabric is composed of a first set of

threads comprising 3.5 to 20 threads/cm and having a titer of at least 420 dtex, and a second set of threads comprising 0.5 to 8 threads/cm and having a titer of at least 50 dtex, which second set of threads is transverse to the first set of threads, and wherein the ratio of the linear density of the first set of threads to the linear density of the second set of threads is > 4.2 , and the ratio of the number of threads/cm of the first set to that of the second set is > 1 , have improved ballistic properties.

Preferably, the penetration-resistant material has a ratio of the linear density of the first set of threads to the linear density of the second set of threads > 7.5 . The number of threads in the first set of threads is 3.5 to 20 threads/cm. More preferably, the number is 4 to 15 threads/cm, and most preferably 5 to 12 threads/cm. The number of threads in the second set of threads is 0.5 to 8 threads/cm. More preferably, the number is 1 to 6 threads/cm, and most preferably 2 to 4 threads/cm. For reasons of efficient manufacturing it is preferred that the first set of threads is of warp threads and the second set of threads is weft threads. The second set of threads is transverse to the first set of threads. Although usually these sets are about perpendicular to each other, this is not necessary. The second set of threads may be provided under at angle other than 90° to the first set of threads.

The penetration-resistant material also consists of a second set of threads (preferably weft threads), the yarn composition of which is not decisive for the present invention. Preferably, however, these threads have high strength and high modulus. This is particularly the case when these threads are selected from polyester, polyethylene, polypropylene, polyamide, and aramid yarn. Most preferably, the second set of threads is made of polyester yarn.

The first set of threads (preferably warp threads) is of high strength and high modulus, and most preferably aramid yarn is selected, more particularly p-aramid. Most preferred is poly para-phenyleneterephthalamide (PPTA). In a preferred embodiment the warp and weft threads are selected to be made of

different polymers, for instance, a fabric having warp threads of p-aramid yarn and weft threads of polyester yarn is preferred.

5 As long as the required linear density ratio is satisfied, the linear density of the first set of threads is selected to be at least about 420 dtex, preferably between 420 and 3360 dtex, more preferably between 420 and 1680 dtex, and most preferably between about 840 and 1100 dtex. The linear density of the second set of threads is selected to be at least about 50 dtex, more preferably between 50 and 280 dtex, and most preferably between about 80 and 140 dtex.

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The term "thread" means any sort of thread such as staple yarn, twisted staple yarn, twisted filament yarn, non-twisted intermingled yarn, and preferably, untwisted filament yarn.

15 In a preferred embodiment the threads of each of the two fabric layers of the double layer are bonded together, for instance, by stitch bonding, or preferably, with an adhesive material. The adhesive material may be adhesive material provided onto the threads or onto the fabric, for instance, as a finish. The adhesive material can also be an adhesive layer provided between the two
20 fabric layers of the double layer. Adhesive materials include thermoplastic, elastomeric, and thermoset materials. It is also possible to use for at least part of the second set of threads a material that melts under pressure and/or heating, thereby accomplishing binding the threads of the first set of threads to those of the second set of threads, and optionally also binding the two fabric
25 layers together. Thermoplastic materials include polyolefins such as polyethylene and polypropylene, polyamide, polyester, or mixtures of these materials. Elastomeric materials include Kraton, rubber, silicon, and the like. Thermoset materials include epoxy resins, polyester resins, phenolic resins, vinyl ester resins, and the like.

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In another preferred embodiment at least one of the outer sides of the penetration-resistant material is provided with a protective layer. The protective

layer can be a thermoplastic or an elastomeric material, or a mixture of these materials. The protective layer is applied to protect the fabric from damage by excessive abrasion.

- 5 The penetration-resistant material comprises at least one double layer consisting of two layers of woven fabric which are cross-plyed at an angle and optionally bonded together. The term woven includes all types of weaves, such as plain weave, satin weave, basket weave, twill weave, and the like. Preferred fabrics are plain woven.

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- The penetration-resistant material may contain as little as one double layer consisting of two layers of woven fabric, but usually more double layers are applied. Suitable numbers of double layers are 5 to 100, and most preferably 6 to 35 double layers are used. In at least one of the double layers the two fabric layers are secured together at an angle. Preferred angles are 30 to 90°. An angle of about 90° is most preferred. For soft armor the best performance is usually obtained when the fabric layers in all double layers are secured at an angle, preferably an angle of 90°. The first set of threads of the first fabric layer of a double layer may be parallel to, or at an angle to, the first set of threads of the first fabric layer of the adjacent double layer.

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The double layers are secured together using an adhesive layer or by stitching. Such an adhesive layer may be made of the previously mentioned materials for the adhesive materials and has a thickness between 4 and 36 μ , preferably between 8 and 20 μ .

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- Methods of manufacture of the double layers are well known in the art. Usually the fabric is made by warping the warp yarn on a beam, followed by weaving on a loom. The single layer may optionally be impregnated or laminated, and be subjected to a calendering process. At least two fabric layers can be bonded together, preferably at an angle to each other, by stitching, heating, or applying pressure.

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The invention pertains also to articles like bulletproof vests and armor plates made of the above-mentioned woven fabric according to methods known to the skilled man.

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The invention is further illustrated with the following examples.

Example 1

Construction I was prepared according to this invention. The construction
10 contained 21 double layers of an about 100 g/m² fabric made from Kevlar®
1100 dtex (ex DuPont) in warp (8.6 threads/cm) and polyester 140 dtex
(Trevira® 710, ex Hoechst) in weft direction (2 threads/cm). The warp/weft ratio
is 7.9. The layers were laminated together with 2 plies of a polyethylene film
(LDPE, ex EKB) having a thickness of 10 µ. The total weight of construction I
15 was about 4300 g/m².

Construction II was prepared according to this invention and contained 20
double layers of the same fabric as used for construction I, and 1 sheet of
polyethylene film (LDPE, ex EKB) having a thickness of 10 µ on both outer
sides of the double layer and in between each of the two fabric layers of the
20 double layer. The total weight of construction II was about 4400 g/m².

V₅₀ values were determined with 9x19 Para Type DM 11 A1B2 bullets, wherein
V₅₀ is the velocity at which 50% of the bullets is stopped and 50% of the bullets
gives full penetration. It was found that V₅₀ of construction I is 471 m/s and that
V₅₀ of construction II is 481 m/s.

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Example 2

Construction III was made analogously to construction I with 19 plies of
Twaron® 930 dtex (CT 709 Microfilament, ex Akzo Nobel) rather than Kevlar
(10.4 warp threads/cm, 2 weft threads/cm, warp/weft ratio 6.6). The total weight
30 of construction III was about 4330 g/m², the V₅₀ (determined with 9x19 Para
Type DM 11 A1B2 bullets) was about 490 m/s.

Comparative Example 3

Construction IV was made from 22 plies of Twaron® fabric style CT 709 (ex Akzo Nobel). Warp and weft threads were made from Twaron® 930 dtex Microfilament (ex Akzo Nobel) (10.5 threads/cm in warp and weft direction; 5 warp/weft ratio 1). The total weight of construction IV was about 4400 g/m², the V₅₀ (determined with 9x19 Para Type DM 11 A1B2 bullets) was about 460-465 m/s.

Example 4

10 Construction V was made from 50 double layers of a fabric made from Twaron® 930 dtex (9,5 threads/cm in warp direction and 2 threads/cm of Trevira 710 140 dtex in weft direction; warp/weft ratio 6.6).

The layers were laminated together with an LDPE-copolymer matrix (resin content 35%) at a temperature of 115°C and a pressure of 2.5 MPa. The total 15 weight was 6500 g/m², the V₅₀ (determined with .357 Magnum FJ CB SC bullets) was 484 m/s.

Comparative Example 5

Construction VI was made from 44 layers of Twaron® CT 709 fabric (930 dtex, 20 200 g/m², plain woven). The material was coated with PVB-modified phenolic resin (resin content 23%) and laminated at a temperature of 160°C and a pressure of 1.0 MPa. The total weight was 10800 g/m², the V₅₀ (determined with .357 Magnum FJ CB SC bullets) was 487 m/s.

By using the above mentioned resin system, resin content, and laminating 25 conditions, the weight could not be reduced without reducing V₅₀.

Claims

1. A penetration-resistant material comprising at least a double layer of fabric composed of two layers of woven fabric which are cross-plyed at an angle, characterized in that the fabric is composed of a first set of threads comprising 3.5 to 20 threads/cm and having a linear density of at least 420 dtex, and a second set of threads comprising 0.5 to 8 threads/cm and having a linear density of at least 50 dtex, with the second set of threads being transverse to the first set of threads, and wherein the ratio of the linear density of the first set of threads to the linear density of the second set of threads is > 4.2 , and the ratio of the number of threads/cm of the first set to that of the second set is > 1 .
2. The penetration-resistant material of claim 1 wherein the threads of the layers of the double layer are bonded together, preferably with an adhesive material.
3. The penetration-resistant material of claim 1 or 2 wherein the ratio of the linear density of the first set of threads to the linear density of the second set of threads is > 7.5 .
4. The penetration-resistant material of any one of claims 1-3 wherein the first set of threads consists of aramid threads.
5. The penetration-resistant material of any one of claims 1-3 wherein the second set of threads is selected from polyester, polyethylene, polypropylene, and aramid yarn.
6. The penetration-resistant material of any one of claims 1-5 wherein the first set of threads consists of aramid threads and the second set of threads consists of polyester threads.

7. The penetration-resistant material of any one of claims 1-6 wherein the linear density of the first set of threads is 420 to 3360, preferably 420 to 1680 dtex, and more preferably 840 to 1100 dtex.
- 5 8. The penetration-resistant material of any one of claims 1-6 wherein the linear density of the second set of threads is 50 to 280 dtex and preferably 80-140 dtex.
- 10 9. The penetration-resistant material of any one of claims 1-8 wherein the first set of threads is warp threads and the second set of threads is weft threads.
10. The penetration-resistant material of any one of claims 1-9 wherein at least one of the outer sides of the material is provided with a protective layer.
- 15 11. An article made of the penetration-resistant material of any one of claims 1-10.

INTERNATIONAL SEARCH REPORT

Inventor's Application No

PCT/EP 00/00290

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D03D15/00 D03D11/00 F41H5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D03D F41H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 229 199 A (MINER) 20 July 1993 (1993-07-20) column 5, line 12 -column 12, line 19 ---	1,2,4,5, 7,9-11
A	US 5 789 327 A (ROUSSEAU) 4 August 1998 (1998-08-04) column 4, line 43 -column 5, line 33; figures 4,5 ---	1,2,4-7, 9,11
A	US 5 275 873 A (CHITRANGAD) 4 January 1994 (1994-01-04) column 3, line 48 -column 4, line 49 ---	1,4,5,7, 9,11
A	US 5 187 003 A (CHITRANGAD) 16 February 1993 (1993-02-16) column 4, line 11 -column 6, line 7 --- -/--	1,4-6,9, 11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Boutelegier, C

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 851 203 A (WRIGHT) 1 July 1998 (1998-07-01) column 6, line 44 - line 53; claims 1-11 ---	1,4,7,9, 11
A	EP 0 310 199 A (STAMICARBON) 5 April 1989 (1989-04-05) cited in the application the whole document ---	1,4,5,9, 11
A	DATABASE WPI Section Ch, Week 9828 Derwent Publications Ltd., London, GB; Class: A23, AN 98-320748 XP002106998 & RU 2 096 542 A (TERLON), 20 November 1997 (1997-11-20) cited in the application abstract -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inventor Application No

PCT/EP 00/00290

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5229199 A	20-07-1993	CA 1335913 A EP 0323541 A ES 2042605 T BR 8800573 A	13-06-1995 12-07-1989 16-12-1993 19-09-1995
US 5789327 A	04-08-1998	NONE	
US 5275873 A	04-01-1994	AU 672271 B AU 5684794 A CA 2150912 A DE 69321738 D DE 69321738 T EP 0695410 A JP 8504503 T WO 9414023 A	26-09-1996 04-07-1994 23-06-1994 26-11-1998 02-06-1999 07-02-1996 14-05-1996 23-06-1994
US 5187003 A	16-02-1993	DE 69207780 D DE 69207780 T EP 0615558 A JP 7501363 T WO 9311290 A	29-02-1996 08-08-1996 21-09-1994 09-02-1995 10-06-1993
EP 851203 A	01-07-1998	GB 2317622 A CA 2216745 A	01-04-1998 28-03-1998
EP 310199 A	05-04-1989	AU 2338088 A BR 8805055 A CN 1035887 A CN 1036418 A JP 1156541 A ZA 8807385 A	06-04-1989 09-05-1989 27-09-1989 18-10-1989 20-06-1989 28-06-1989
RU 2096542 A	20-11-1997	NONE	